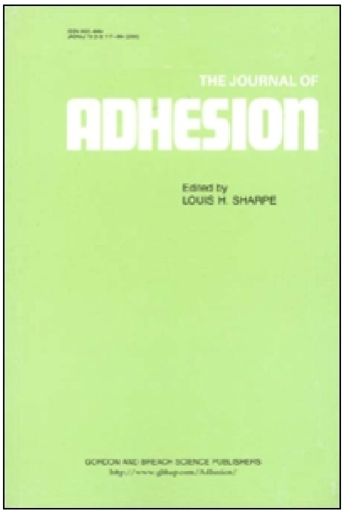

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K. W. Allen[a]; H. S. Alsalim[a]; W. C. Wake[a]
[a] The City University, London, England

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Bonding of Titanium Alloys†

K. W. ALLEN, H. S. ALSALIM and W. C. WAKE

The City University, St. John Street, London, England.

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Surface pretreatments affect joint strength, some improve it, e.g. etching in aqueous hydrofluoric acid or oxidation in alkaline hydrogen peroxide; while others decrease the strength e.g. etching in acids containing high concentrations of oxidising agents.

For Ti-6Al-4V alloy, best results are obtained by either etching in aqueous hydrofluoric acid or oxidation in alkaline hydrogen peroxide for about two hours.

The results indicate that a pretreatment which leaves a coherent TiO_2-rutile layer, on a rough surface, form the strongest joints. Surface roughness is shown to enhance bond strength.

INTRODUCTION

There are several recipes[1,2] for treating titanium and its alloys in preparation for adhesive bonding. These consist basically of hydrofluoric acid and an oxidant and the choice of additives seems to be based on trial and error. These reagents have been examined in detail in terms of the roughness they produce and the nature of the coating they leave on titanium alloys. A new recipe has been advanced; oxidation in alkaline hydrogen peroxide.

The various effects have been studied with two commercially available adhesives known to give high strength with titanium alloys.

MATERIALS AND APPARATUS

The titanium alloy used was exclusively the Ti-6Al-4V alloy (IMI-318, Imperial Metals Industries Ltd., Birmingham). The effect of the various pretreatments was investigated with two adhesives; Redux BSL-308, said to be a modified epoxy adhesive containing aluminium powder as a filler together

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with carbon black, and Hidux 1197C, a modified epoxy—phenolic material supported on glass cloth and containing aluminium powder as well. Both adhesives are products of Ciba-Geigy Ltd., Duxford, Cambridge.

Two methods of testing were employed; tensile and torsional shear. Tensile testing was carried out using Instron—model 1026 and single laps measuring 5 × (0.7–0.8) × 0.2 cm with an overlap of 1 cm, giving a bonded area of about 0.8 sq. cm. This rather small area was necessary to accommodate the test pieces within the tensile range of the Instron.

Torsional shear testing was carried out using napkin-ring test pieces and a Wallace torsional shear adhesive test apparatus.[3] These have been described elsewhere.[4-6] In the present work, all calculations assumed elastic failures as the error is of no consequence since absolute stress values are not discussed.

TITANIUM ALLOY IMI-318

This alloy consists of 90 percent titanium, 6 percent aluminium and 4 percent vanadium[7] and is an alpha and beta alloy, which in the samples obtained, had alpha/beta ratio of about 70/30. The presence of the two phases played a principal role in dictating the final topographical features obtained by any pre-treatment. This is because of the existing differences in their reactivities in any medium.

PRETREATMENTS OF IMI-318 ALLOY

To understand the effect of the various pretreatments investigated, the nature as well as the morphology of the adherends were examined by several techniques including X-ray powder diffraction, transmission and reflection electron diffraction, and transmission electron microscopy.

The effect of the following pretreatments were investigated:

i) Etching in aqueous 4 percent w/v hydrofluoric acid solution.
ii) Etching in 4 percent w/v hydrofluoric acid in a saturated aqueous solution of oxalic acid.
iii) Effect of adding nitric acid to hydrofluoric acid.
iv) Oxidation in alkaline hydrogen peroxide.

The differences between treatment (i) and (ii) were that the latter is slower in attack but the final topographical features obtained by both treatments are almost identical except that treatment (ii) produced a smoother surface.

Results[8] obtained with electron diffraction showed that the only crystalline compound formed at the surface after these four pretreatments is TiO_2-rutile. The mode of attack by hydrofluoric acid in treatments (i)–(iii) is the same. The alpha phase is attacked preferentially leaving beta phase protruding and it is easily seen that the optimum roughness is dictated by the

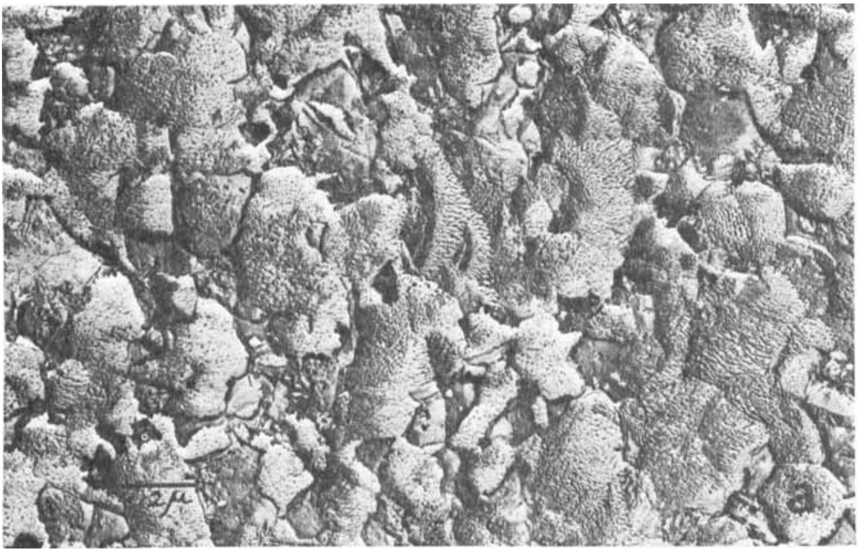
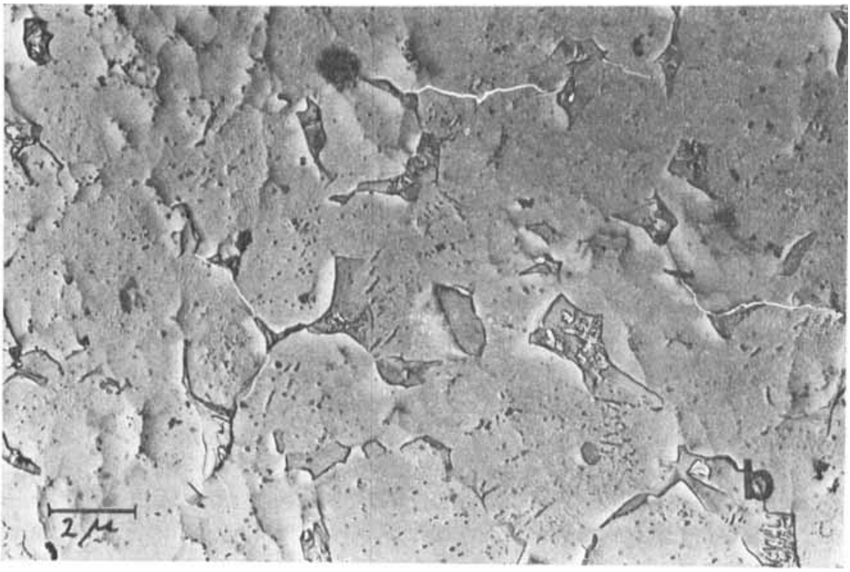


FIGURE 1 Electron micrographs (original mag. 2,500) of Ti-6Al-4V alloy etched for 1½ minutes in:
(a) —4 percent w/v hydrofluoric acid



(b) —4 percent w/v hydrofluoric acid containing 10 percent w/v nitric acid.
These show the effect of nitric acid in producing a smoother surface.

area of individual patches as well as the total area of the beta phases. The presence of oxidising agents such as nitric acid in hydrofluoric acid solutions slows down reaction, leading to smoother surfaces because nitric acid oxidises the surface and in the presence of an oxide layer preferential attack is reduced. Figure 1 shows the effect of addition of 10 percent w/v nitric acid to 4 percent w/v hydrofluoric acid on the final roughness obtained.

Alkaline solutions of hydrogen peroxide have the ability to act simultaneously as oxidising and corroding agents. Depending on the concentrations; titanium alloy either becomes passive and is coated by a protective, glossy and translucent film; or is coated by an oxide whose colour varies from yellow, mauve, blue, grey, to black; or is quickly corroded. Close examination of oxidised specimens in various solutions indicated that solutions leading to formation of a black oxide formed the roughest surface. The mode of attack on the alloy phases is rather complex and prolonged oxidation leads to highly porous and weakly coherent oxide layers.

ETCHING IN HYDROFLUORIC ACID AND BOND STRENGTH

The effects of etching in 4 percent w/v hydrofluoric acid with and without oxalic acid are illustrated in Figure 2. This was investigated with the modified epoxy adhesive, Redux, BSL-308 using single lap joints. The etched specimens were washed with water and rinsed with acetone before drying at 100°C.

In spite of the large scatter indicated, it is apparent that an etch time of greater than $1\frac{1}{2}$ minutes is desirable. The apparent decrease in joint strength with prolonged etching is due to dissolution of the sharp edges around the areas to be bonded, leading to formation of a wedge. The mode of failure was mainly cohesive within the adhesive.

Confirmation of the time of etching was sought with another adhesive and with the torsional shear napkin ring test pieces. The adhesive used for bonding them was Hidux 1197C, a modified epoxy—phenolic material supported on glass cloth. The results are shown in Figure 3, and in spite of the apparent scatter the spread is far less than with the lap joints shown in Figure 2. Moreover, the line shown is a calculated fit to the equation $y = A - (B/X)$ $(x > 0)$ where y is the bond strength, x is the time of etching, and A and B are constants. As with lap joint strengths, change is slight after $1\frac{1}{2}$ minutes; doubling the etching time increases the bond strength by about 1 percent.

Bond failure was not the same over the range investigated; bonds made with rings etched for less than $1\frac{1}{2}$ minutes failed mainly at the interface while those etched for longer times failed cohesively within the adhesive. In some cases substrate failure was seen clearly, particularly with specimens etched for longer than 3 minutes. Careful examination of broken joints revealed the

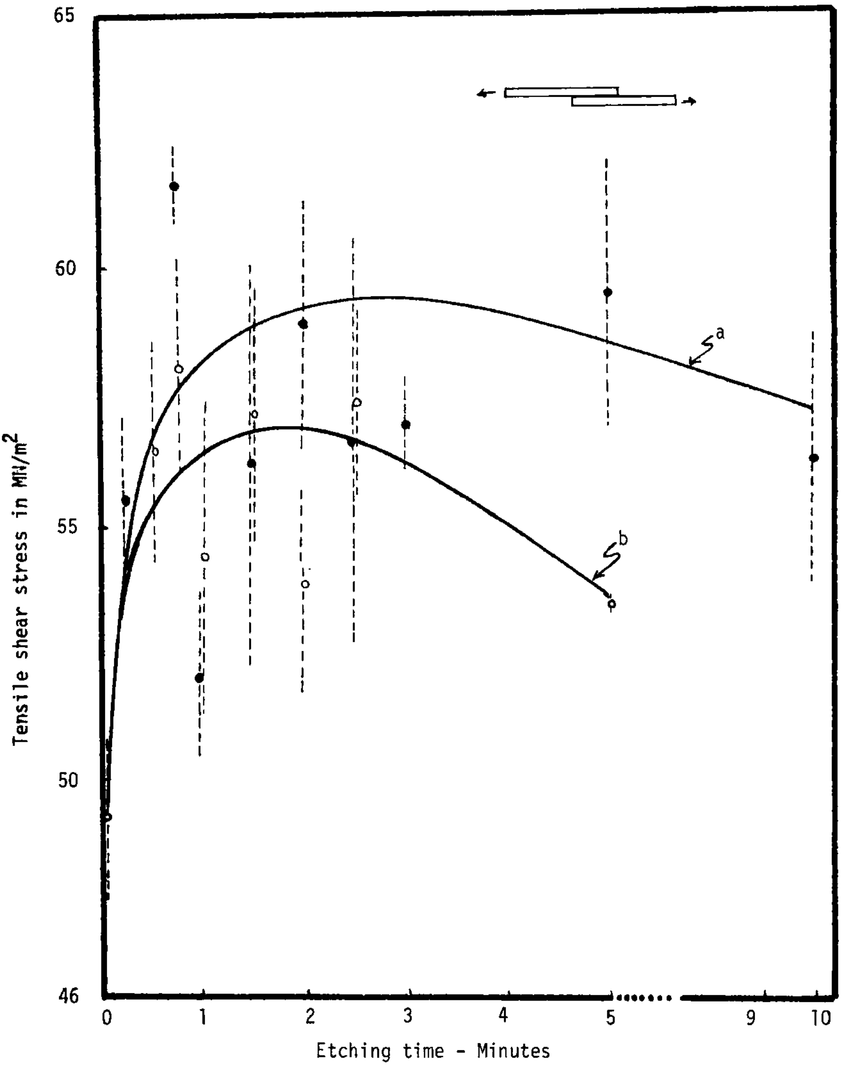


FIGURE 2 Effect of etching with aqueous hydrofluoric acid (4 percent w/v) (●—curve a) and hydrofluric acid (4 percent w/v) in saturated oxalic acid aqueous solution (○—curve b) for various times on bond strength.

presence of a filler-free layer of adhesive between the substrate and the bulk of adhesive bond.

As pointed out earlier, the presence of oxidising agents such as nitric acid in hydrofluoric acid solutions slows down the reaction, leading to smoother surfaces. The effect on bond strength of adding nitric acid to 4 percent w/v

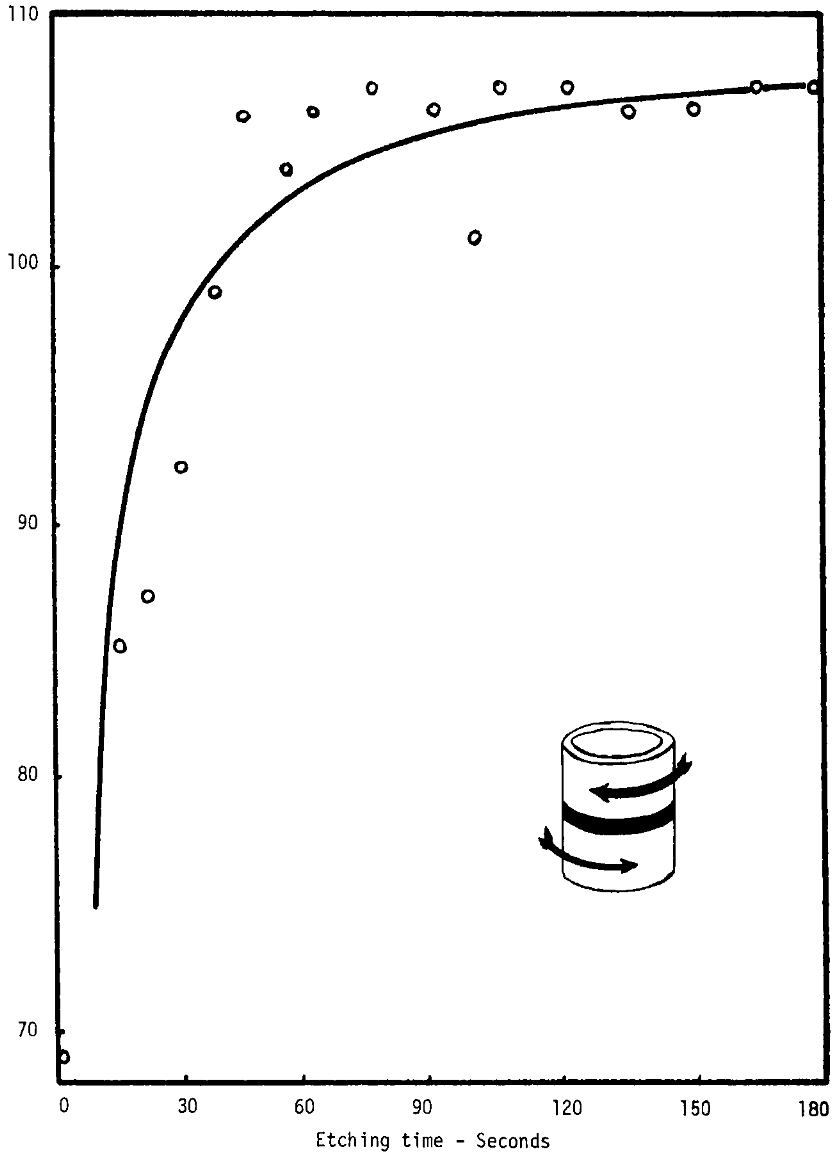


FIGURE 3 Effect of etching with hydrofluoric acid (4 percent w/v) for various times on bond strength.

hydrofluoric acid solution was also investigated using napkin ring test pieces and Hidux 1197C adhesive. The test pieces were treated for 1½ minutes, an appropriate time as indicated by Figure 3. The results are shown in Figure 4.

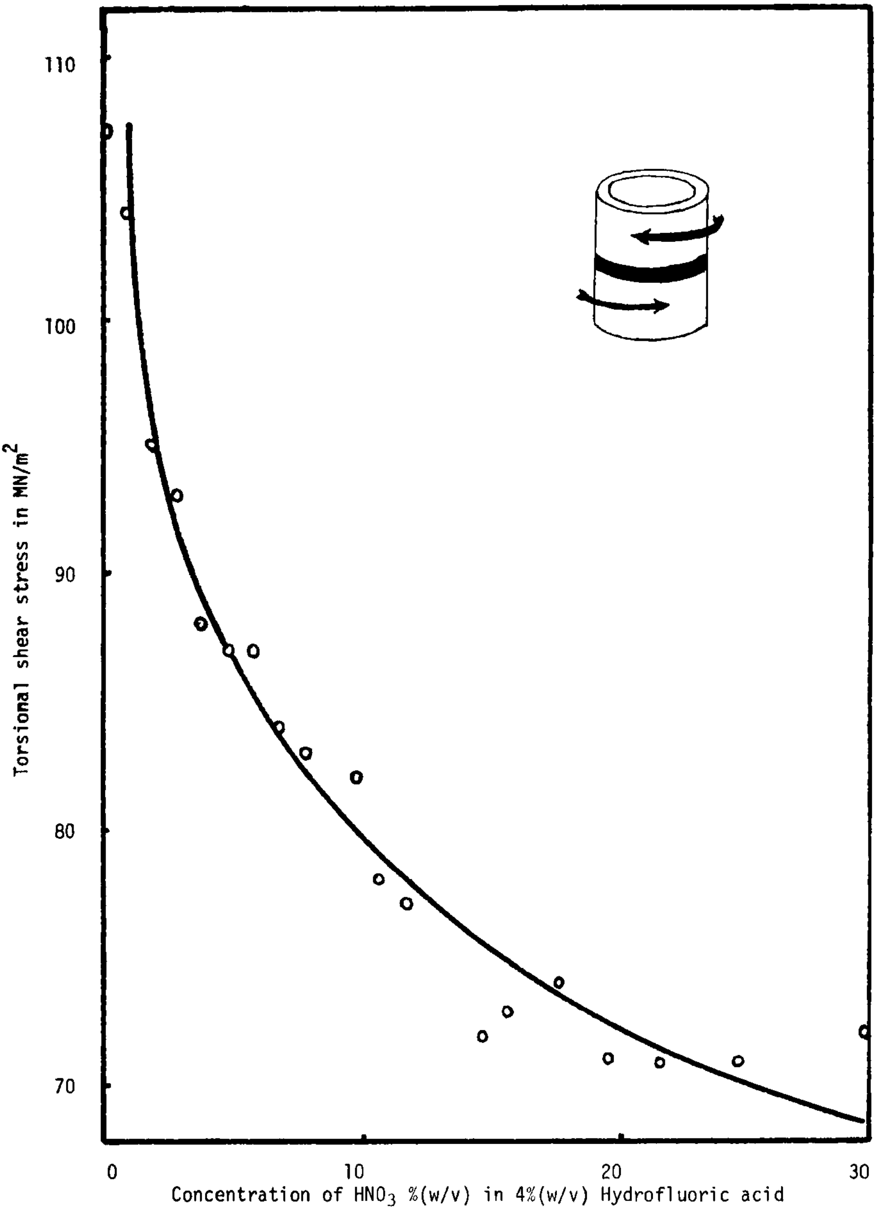


FIGURE 4 Effect of addition of nitric acid to (4 percent w/v) hydrofluoric acid on joint strength.

They indicate that addition of nitric acid leads to weaker joints which tend to a limiting value ca.71 MN/m^2 at concentrations greater than 20 percent w/v of nitric acid. It is interesting to note that the mode of failure changed from about 100 percent cohesive within the adhesive at low concentrations of nitric acid, to almost completely interfacial at high concentrations, as far as can be detected by electron microscopy. Where failure was cohesive, the position of failure within the adhesive bond depended on the concentration of nitric acid. The distance of the fracture from the interface decreased with increase in nitric acid concentration. Some substrate failure was observed but it was confined to adherends etched in solutions containing less than 3 percent w/v nitric acid. The magnitude of failure was of the same order as that observed with adherends etched in aqueous hydrofluoric acid for longer than 1½ minutes.

The relationship between joint strength and concentration of nitric acid is given by:

$$y = m \log C$$

where y is bond strength, C is concentration of nitric acid added and m is constant.

A plot of y against log C shows a good linear relationship between bond strength and concentration of nitric acid.

An important feature of this experiment is the decreasing roughness of the alloy surface as the attack by hydrofluoric acid is controlled and inhibited by the oxidant present. This provides strong evidence that high bond strength is associated with some degree of mechanical interlocking with the adherend surface. The very smooth surfaces resulting from the higher concentrations of nitric acid are not only those of lower strength but are also those where failure seems almost certainly to be interfacial.

OXIDATION IN ALKALINE HYDROGEN PEROXIDE AND BOND STRENGTH

The effect of oxidation time in alkaline hydrogen peroxide on bond strength using lap joints and Redux BSL-308 adhesive was investigated for the region of black oxide formation. Laps were oxidised at room temperature in a solution containing 0.04 M hydrogen peroxide and 0.24 M sodium hydroxide. The oxidised laps were washed with water and acidified water before they were given an acetone rinse and dried at 100°C. Figure 5 shows that strong joints can be obtained by short periods of oxidation. The observed decrease in bond strength with oxidation time is due to two main reasons. First, the surface becomes porous and when the entrapped gases expand during curing of the adhesive, bubbles appear within the adhesive bond. These bubbles were

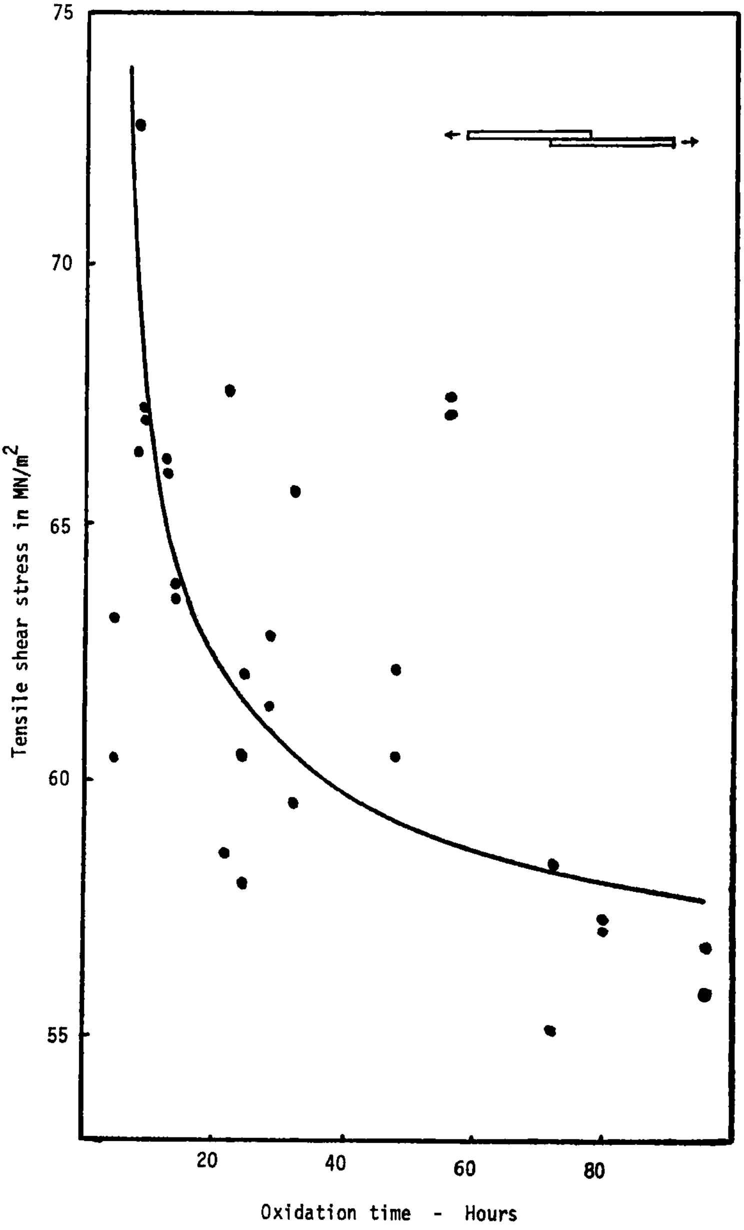


FIGURE 5 Effect of oxidation for various times in hydrogen peroxide (0.24 M) solution (Black oxide region) on bond strength.

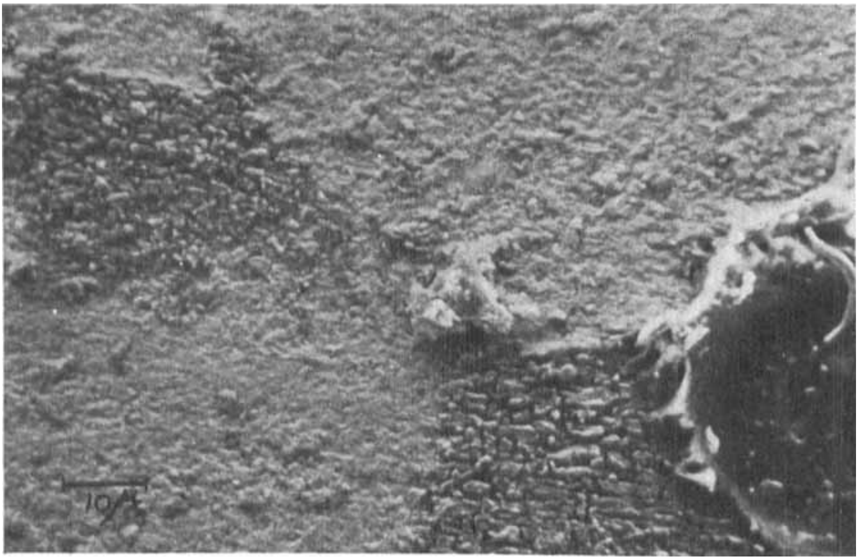


FIGURE 6 Stereo electron micrograph (original mag. 1000) of a fractured joint showing substrate failure.

seen to form with specimens oxidised for longer than 10 hours. Second, the thick oxide layer formed on specimens oxidised for longer than 48 hours is weakly coherent. In fact substrate failure on a large scale was observed with all specimens oxidised for longer than 48 hours. Figure 6 shows a region where substrate failure took place.

The scatter in Figure 5 is large but the line shown in the figure is a reasonable fit by least squares method to an equation:

$$y = A/x + B, \qquad (x > 0)$$

where y is bond strength and x is oxidation time.

DISCUSSION

These experiments illustrate that surface pretreatments do affect bond strength; some improve bond strength while others decrease the strength. It is for this reason that it is necessary to establish the optimum conditions for surface treatment.

In all these treatments, the only crystalline compound which is formed on the adherend is TiO_2-rutile. The differences between these treatments is that the oxide layer formed differs in its coherency. No hydride[9] or fluoride[10] was detected with the rutile. The topography of the adherend together with the coherency of the oxide formed are the two factors deciding the optimum conditions. For the pretreatments investigated the optimum conditions are:

i) For etchants containing hydrofluoric acid with or without an oxidant the specimens should be etched for at least 1½ minutes. If an oxidant must be added to the etchant then the smallest possible amount should be added.

ii) For oxidation in alkaline hydrogen peroxide, an oxidation time between 1–2 hours is desirable, but the exact concentration of peroxide and alkali required to obtain maximum roughness must be found for each alloy. For Ti-6Al-4V (IMI-318) alloy these are 0.04 M hydrogen peroxide and 0.24 M sodium hydroxide.

There are many recipes in the literature for pretreating titanium and its alloys but it seems that they are based on trial and error. The basic item in these recipes is a reducing acid and any other additive is there to prevent or rather minimise hydrogen pick up which causes enbrittlement of the alloy. If a recipe leads to strong bonds with one alloy, it does not mean that it will necessarily do so for a different alloy. For example, aqueous hydrofluoric acid leads to an increase in bond strength with IMI-318 (Ti-6Al-4V) alloy but when used to etch IMI-205 (Ti-15Mo) a decrease in bond strength is observed due to the formation of loose molybdenum oxide on the surface. To remove this black and loose oxide large amounts of nitric acid are required in the recipe but such solutions leave a very smooth surface.

The observed change in mode of failure with Hidux 1197C adhesive on adherends treated according to pretreatments (i) and (ii) indicates that mecanical adhesion is taking place, since smooth surfaces lead to interfacial failure while rough surfaces to cohesive failure within the adhesive.

The presence of the filler-free material at the interface is caused possibly by migration of a low molecular weight component towards the interface during setting of the adhesive.

It follows therefore that in order to obtain maximum bond strength with titanium alloys a pretreatment which leaves a coherent oxide layer on the surface must be selected and the treated alloy must have a rough surface. The latter can be achieved by using etchants in which the difference between the rates of attack on the alpha and beta phases of the alloy is maximum.

It is also desirable to use as little as possible of oxidant with a reducing acid.

Acknowledgement

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